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LETTER TO THE EDITOR

Atomic-charge log-convexity and radial expectation values

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Abstract. Let us denote by $\rho(r)$ the spherically averaged electron density of an atomic system. First, it is found that there always exists a parameter $\alpha_0 \geqslant 0$ such that the function $\rho(r)/r^{\alpha}$ is logarithmically convex for any $\alpha \geqslant \alpha_0$. Furthermore, $\alpha_0 \geqslant \max\{\beta, 0\}$ with $\beta = 2(1/\sqrt{2I} - 1)$, I being the ionization potential. Secondly, such a property is used to obtain rigorous and compact inequalities involving three radial expectation values, which substantially generalize all the similar ones known up to now. These inequalities allow us to correlate several fundamental and/or measurable physical quantities such as the nuclear electron attraction energy, the Langevin–Pauli diamagnetic susceptibility and so on. Thirdly, the log-convexity property is investigated in a Hartree–Fock framework for all ground-state neutral atoms with $Z \leqslant 54$. In particular, it is found that all the atoms have a log-convex function $\rho(r)/r^6$ and only H and He have a log-convex electron density $\rho(r)$. Finally, the accuracy of the above-mentioned inequalities is studied in the same numerical framework.

The study of the structural properties other than positivity of the single-fermion density $\rho(r)$ is a basic problem for all many-fermion systems in its own right and because it is of its great help to the practical and formal approaches of the modern density-functional theory. In the case of a N-electron system, where this problem is best controlled, the only rigorous information about the electron density $\rho(r)$ of the ground state which one encounters in the literature (Parr and Yang 1989, Kryachko and Ludeña 1989, Dreizler and Gross 1990) is its behaviour near the origin (Kato 1957, Steiner 1963, Smith 1971) and at large distances (Morrell *et al* 1975, Ahlrichs 1976, Hoffmann-Ostenhof *et al* 1978, Alhrichs *et al* 1981, Silverstone 1981). In addition, from a numerical point of view, one knows that the spherically-averaged electron density $\rho(r)$ defined as

$$\rho(r) \equiv \frac{1}{4\pi} \int \rho(r)\, \mathrm{d}\Omega$$

is (i) monotonically decreasing from the origin (Sperber 1971, Weinstein *et al* 1975, Simas *et al* 1988, Angulo 1989) for all ground-state neutral atoms, from hydrogen to uranium, (ii) convex (Angulo *et al* 1990) for the atoms with Z = 1,2,7–15 and 33–44 while for the rest of the atoms up to $Z = 54$ it presents a very small non-convex region. Furthermore, the complete monotonicity of the function $\rho(r)$ was recently studied (Angulo and Dehesa 1991); we found that such a property is fulfilled for all neutral atoms below Xe to a reasonably good approximation, except for hydrogen where it is rigorous.

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Here we will study the logarithmic convexity of $\rho(r)$, which is a property stronger than convexity but weaker than complete monotonicity. Since $\rho(r)$ is not universally convex (Angulo *et al* 1990), it will not be logarithmically convex, or shortly log-convex, for all neutral atoms. So, in looking for properties of $\rho(r)$ valid for the whole periodic table, we will analyse the log-convexity of the atomic electron function $g_\alpha(r) \equiv r^{-\alpha}\rho(r), \alpha \geqslant 0$, i.e. the non-negativity of the function

$$h(r) = \frac{d^2 \ln g_\alpha(r)}{dr^2} = \frac{d^2}{dr^2}\left(\ln \frac{\rho(r)}{r^\alpha}\right)$$

and some physical consequences which are expressed via inequalities among radial expectation values.

From the inequality $h(r) \geqslant 0$ one directly observes that for each atomic system described by the density $\rho(r)$ there always exists a minimal value $\alpha_0 \geqslant 0$ given by

$$\alpha_0 = \max\left\{-r^2 \frac{d^2 \ln \rho(r)}{dr^2}\right\} \tag{1}$$

such that for any $\alpha \geqslant \alpha_0$ the density function $g_\alpha(r)$ is logarithmically convex. Taking into account that the asymptotic behaviour of $\rho(r)$ is like $r^\beta \exp(-\sqrt{8I}\, r)$, where I is the first ionization potential and $\beta = 2(1/\sqrt{2I} - 1)$, one has that $\alpha_0 \geqslant \max\{\beta, 0\}$ (Tal 1978).

To have an idea about the value of α_0, we have calculated it by means of the near-Hartree–Fock atomic wavefunctions of Clementi and Roetti (1974) for all neutral atoms with $Z \leqslant 54$. In doing so, care has been taken about the non-reliability of the corresponding ground-state density by considering the above mentioned physical behaviour of $\rho(r)$ at large distances. The numerical results of α_0 are shown in table 1. Therein one notices that: (i) the only atoms with a log-convex electron density $\rho(r)$ are hydrogen, where it is rigorous, and helium, (ii) for atoms with a nuclear charge Z, such that $3 \leqslant Z \leqslant 14$, α_0 varies from 1.39 to 2.81 and (iii) for atoms with $Z \geqslant 15$, α_0 is always bigger than 3.00 without any monotonic behaviour; its maximum value is 5.98 for xenon ($Z = 54$).

The specific behaviour of α_0 can be seen more transparently in figure 1 where the data contained in table 1 are shown. A simple phenomenological fit for α_0 in terms of Z has not been found.

Since $\ln g_\alpha(r)$ is convex for some α, then $\ln \lambda_p$ is also convex (Karlin *et al* 1961) for $p \geqslant 0$. Here λ_p denotes the quantities

$$\lambda_p \equiv \frac{\mu_p}{\Gamma(p+1)} \tag{2}$$

where $\Gamma(x)$ denotes the well known gamma function, and μ_p are the moments around the origin of the density function $g(r)$ given by

$$\mu_p \equiv \int_0^\infty r^p g(r)\, dr = \int_0^\infty r^{p-\alpha}\rho(r)\, dr = \frac{1}{4\pi}\langle r^{p-\alpha-2}\rangle \qquad \text{for } p > \alpha - 1. \tag{3}$$

Here the symbol $\langle r^m \rangle$ denotes the mth radial expectation value defined as

$$\langle r^m \rangle \equiv \int r^m \rho(\boldsymbol{r})\, d\boldsymbol{r}.$$

Table 1. Values of α_0 for all neutral atoms, $1 \leqslant Z \leqslant 54$, obtained with Clementi–Roetti near-Hartree–Fock wavefunctions. The atomic density function $\rho(r)/r^{\alpha}$, $\alpha \geqslant \alpha_0$, is logarithmically convex. Atomic units are used throughout.

Z	α_0	Z	α_0	Z	α_0
1	0.0000	19	3.9494	37	3.4639
2	0.0000	20	4.2373	38	3.5684
3	2.7431	21	4.1098	39	3.6047
4	2.7084	22	3.9401	40	3.6571
5	2.2582	23	3.7982	41	3.7158
6	1.9327	24	3.4283	42	3.7468
7	1.7092	25	3.5365	43	3.9738
8	1.5254	26	3.4219	44	4.0046
9	1.3941	27	3.2938	45	4.1588
10	1.2965	28	3.1862	46	4.1865
11	2.4582	29	2.9448	47	4.4162
12	2.3795	30	2.9932	48	4.7968
13	2.4344	31	3.0288	49	4.9590
14	2.8070	32	3.0870	50	5.1682
15	3.1354	33	3.1617	51	5.3942
16	4.0266	34	3.2056	52	5.5969
17	3.4319	35	3.3330	53	5.7778
18	3.5745	36	3.4184	54	5.9802

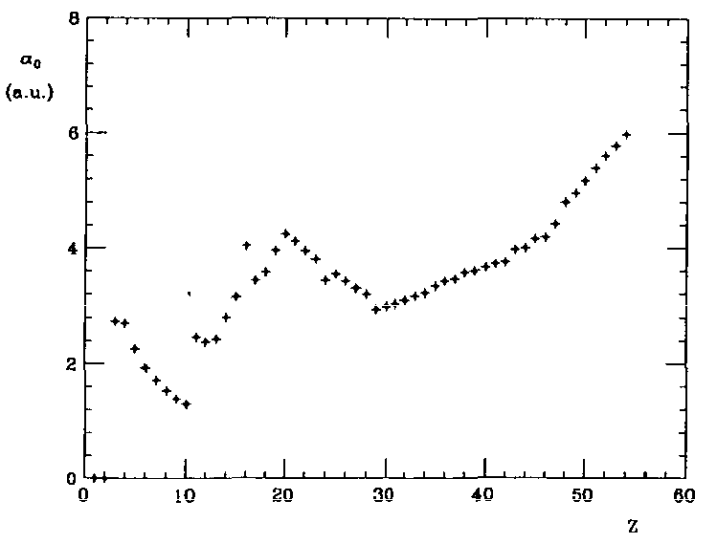

Figure 1. Values of α_0 in terms of the nuclear charge Z for all neutral atoms, $1 \leqslant Z \leqslant 54$, obtained with Clementi–Roetti near-Hartree–Fock wavefunctions. The atomic density function $\rho(r)/r^{\alpha}$, $\alpha \geqslant \alpha_0$, is logarithmically convex. Atomic units are used throughout.

The log-convexity of λ_p means (Roberts and Varberg 1972) that these quantities satisfy the inequalities

$$\lambda_{ap+bq} \leqslant \lambda_p^a \lambda_q^b$$

for $p \geqslant 0$, $q \geqslant 0$ and $a > 0$, $b > 0$ provided that $a + b = 1$.

Taking into account (2) and (3), this inequality transforms into the following general relationship among radial expectation values:

$$\frac{\langle r^{ap+bq-\alpha-2}\rangle}{\Gamma(ap+bq+1)} \leqslant \left[\frac{\langle r^{p-\alpha-2}\rangle}{\Gamma(p+1)}\right]^a \left[\frac{\langle r^{q-\alpha-2}\rangle}{\Gamma(q+1)}\right]^b \tag{4}$$

which is valid for any many-electron system with $\alpha \geqslant \alpha_0$ and the above mentioned values of p, q, a and b. This relationship generalizes and improves the accuracy of all the similar atomic inequalities previously published (Tsapline 1970, Blau *et al* 1973, Gadre 1979).

The richness of this relationship will be illustrated by taking into account the case $p > q$ with $p = q + 2m$ and $m \geqslant 0$. Then, (4) becomes

$$\frac{\langle r^{n+2am-2}\rangle}{\Gamma(n+\alpha+2am+1)} \leqslant \left[\frac{\langle r^{n+2m-2}\rangle}{\Gamma(n+\alpha+2m+1)}\right]^a \left[\frac{\langle r^{n-2}\rangle}{\Gamma(n+\alpha+1)}\right]^{1-a} \tag{5}$$

where $0 < a < 1$, $\alpha \geqslant \alpha_0$ and $n = q - \alpha \geqslant -\alpha$. Let us consider several sets of inequalities contained in this relationship:

A. For $a = \frac{1}{2}$, (5) reduces as

$$\langle r^{n+2m-2}\rangle\langle r^{n-2}\rangle \geqslant \frac{\Gamma(n+\alpha+2m+1)\Gamma(n+\alpha+1)}{[\Gamma(n+\alpha+m+1)]^2}\langle r^{n+m-2}\rangle^2 \tag{6}$$

with $m \geqslant 0$, $\alpha \geqslant \alpha_0$ and $n \geqslant -\alpha$. Here, we will analyse in detail only the subcases $m = 1$ and 2.

A_1. If $m = 1$, then (6) simplifies as:

$$\langle r^n\rangle\langle r^{n-2}\rangle \geqslant \frac{n+\alpha_0+2}{n+\alpha_0+1}\langle r^{n-1}\rangle^2 \qquad \text{for } n \geqslant -\alpha_0 \tag{7}$$

where one has already considered that for a fixed n the best bound corresponds to the value $\alpha = \alpha_0$. Subcases of (7) are:

$$N\langle r^{-2}\rangle \geqslant \frac{\alpha_0+2}{\alpha_0+1}\langle r^{-1}\rangle^2 \tag{8}$$

$$\langle r\rangle\langle r^{-1}\rangle \geqslant \frac{\alpha_0+3}{\alpha_0+2}N^2 \tag{9}$$

$$\langle r^2\rangle N \geqslant \frac{\alpha_0+4}{\alpha_0+3}\langle r\rangle^2 \tag{10}$$

$$\langle r^3\rangle\langle r\rangle \geqslant \frac{\alpha_0+5}{\alpha_0+4}\langle r^2\rangle^2 \tag{11}$$

which are more accurate than the corresponding bounds known up to now (Gadre 1979), at least for all the ground-state neutral atoms up to Xe.

It is interesting to recall here the inequality

$$\langle r^n\rangle\langle r^{n-2}\rangle \geqslant \frac{(n+2)^2}{(n+1)(n+3)}\langle r^{n-1}\rangle^2 \qquad \text{with } n > -1 \tag{12}$$

recently obtained by the authors (Angulo and Dehesa 1991) with only the assumption of monotonically decreasing behaviour (also called unimodality with mode at the origin or monotonicity of first degree or, simply, monotonicity) for the electron density $\rho(r)$. Subcases of (12) are

$$N\langle r^{-2}\rangle \geqslant \tfrac{4}{3}\langle r^{-1}\rangle^2 \tag{13}$$

$$\langle r\rangle\langle r^{-1}\rangle \geqslant \tfrac{9}{8}N^2 \tag{14}$$

$$\langle r^2\rangle N \geqslant \tfrac{16}{15}\langle r\rangle^2 \tag{15}$$

$$\langle r^3\rangle\langle r\rangle \geqslant \tfrac{25}{24}\langle r^2\rangle^2 \tag{16}$$

The comparison between (7) and (12) shows that, for a given n, the lower bound (7) is higher, and so better, than the corresponding one given by (12) for the atomic systems with

$$\alpha_0 < (n+2)(n+1).$$

In particular, this tells you that (i) the inequality (8) is more accurate than that given by (13) for all N-electron systems where $\alpha_0 < 2$, as occurs in the neutral atoms with $Z=1,2$ and 6–10, and (ii) the inequalities (7) with $n \geqslant 1$, such as e.g. those given by (9), (10) and (11), are more accurate than the corresponding ones (12), together which those given by (14), (15) and (16), for all neutral atoms, hydrogen to xenon. This comparison seems to indicate that the log-convexity of the atomic electron function $\rho(r)/r^{\alpha_0}$ is, generally speaking, a stronger property than that of the monotonic decreasing of the electron density $\rho(r)$.

Even more interesting is the comparison of the inequality (7) based on the log-convexity of the atomic function $\rho(r)/r^{\alpha_0}$ with the recently found inequality (Angulo and Dehesa 1991)

$$\langle r^n\rangle\langle r^{n-2}\rangle \geqslant \frac{(n+2)(n+3)}{(n+1)(n+4)}\langle r^{n-1}\rangle^2 \qquad \text{with } n > -1 \tag{17}$$

obtained with the assumption of convexity for the electron density $\rho(r)$. Subcases of (17) are:

$$N\langle r^{-2}\rangle \geqslant \tfrac{3}{2}\langle r^{-1}\rangle^2 \tag{18}$$

$$\langle r\rangle\langle r^{-1}\rangle \geqslant \tfrac{6}{5}N^2 \tag{19}$$

$$\langle r^2\rangle N \geqslant \tfrac{10}{9}\langle r\rangle^2 \tag{20}$$

$$\langle r^3\rangle\langle r\rangle \geqslant \tfrac{15}{14}\langle r^2\rangle^2. \tag{21}$$

This comparison shows that for a given n the lower bound (7) is more accurate than the corresponding one given by (17) for those atomic systems having

$$\alpha_0 < \tfrac{1}{2}(n+2)(n+1). \tag{22}$$

A few observations may now be made.

(i) The inequality (8) is more accurate than (18) for all N-electron systems with $\alpha_0 < 1$. The only neutral atoms satisfying this condition are H and He, where $\alpha_0 = 0$, i.e. the electron density $\rho(r)$ is logarithmically convex from the nucleus.

(ii) The inequality (9) is more accurate than (19) for every N-electron system with $\alpha_0 < 3$. All the neutral atoms, hydrogen to silicon, as well as copper and zinc fulfil this condition.

(iii) The inequalities (7) with $n \geqslant 2$, of which (8) and (9) are two instances, are more accurate than the corresponding convexity-based inequalities (17), of which (20) and (21) are again two particular subcases, for those many-electron systems satisfying the associated condition (22). All neutral atoms, hydrogen to xenon, belong to this class of electron systems.

These observations show that the accuracy of the inequalities based on the logarithmic convexity of $\rho(r)/r^{\alpha_0}$ is greater than that of those based on the convexity of $\rho(r)$ for both light and heavy atoms unless an expectation value of negative order is involved.

A_2. If $m = 2$, then (6) transforms into

$$\langle r^{n+2}\rangle\langle r^{n-2}\rangle \geqslant \frac{(n+\alpha_0+4)(n+\alpha_0+3)}{(n+\alpha_0+2)(n+\alpha_0+1)}\langle r^n\rangle^2 \qquad \text{for } n \geqslant -\alpha_0. \tag{23}$$

Some important subcases are:

$$\langle r^2\rangle\langle r^{-2}\rangle \geqslant \frac{(\alpha_0+4)(\alpha_0+3)}{(\alpha_0+2)(\alpha_0+1)}N^2 \tag{24}$$

$$\langle r^3\rangle\langle r^{-1}\rangle \geqslant \frac{(\alpha_0+5)(\alpha_0+4)}{(\alpha_0+3)(\alpha_0+2)}\langle r\rangle^2 \tag{25}$$

$$\langle r^4\rangle N \geqslant \frac{(\alpha_0+6)(\alpha_0+5)}{(\alpha_0+4)(\alpha_0+3)}\langle r^2\rangle^2. \tag{26}$$

B. For $a = \frac{1}{4}$, (5) reduces to

$$\langle r^{n+2m-2}\rangle\langle r^{n-2}\rangle^3 \geqslant \frac{\Gamma(n+\alpha+2m+1)\,[\Gamma(n+\alpha+1)]^3}{[\Gamma(n+\alpha+m/2+1)]^4}\langle r^{n+m/2-2}\rangle^4 \tag{27}$$

with $m \geqslant 0$, $\alpha \geqslant \alpha_0$ and $n \geqslant -\alpha_0$. In particular, for $m = 2$ one has

$$\langle r^{n+2}\rangle\langle r^{n-2}\rangle^3 \geqslant \frac{(n+\alpha_0+4)(n+\alpha_0+3)(n+\alpha_0+2)}{(n+\alpha_0+1)^3}\langle r^{n-1}\rangle^4 \qquad \text{for } n \geqslant -\alpha_0 \tag{28}$$

where, again, we have considered that for a fixed n the value $\alpha = \alpha_0$ gives the best bound. Some important subcases are:

$$\langle r^2\rangle\langle r^{-2}\rangle^3 \geqslant \frac{(\alpha_0+4)(\alpha_0+3)(\alpha_0+2)}{(\alpha_0+1)^3}\langle r^{-1}\rangle^4 \tag{29}$$

$$\langle r^3\rangle\langle r^{-1}\rangle^3 \geqslant \frac{(\alpha_0+5)(\alpha_0+4)(\alpha_0+3)}{(\alpha_0+2)^3}N^4 \tag{30}$$

$$\langle r^4\rangle N^3 \geqslant \frac{(\alpha_0+6)(\alpha_0+5)(\alpha_0+4)}{(\alpha_0+3)^3}\langle r\rangle^4. \tag{31}$$

C. For $a = \frac{1}{3}$, (5) reduces as

$$\langle r^{n+2m-2}\rangle\langle r^{n-2}\rangle^2 \geqslant \frac{\Gamma(n+\alpha+2m+1)\,[\Gamma(n+\alpha+1)]^2}{[\Gamma(n+\alpha+2m/3+1)]^3}\langle r^{n+2m/3-2}\rangle^3 \tag{32}$$

with $m \geqslant 0$, $\alpha \geqslant \alpha_0$ and $n \geqslant -\alpha_0$. An important particular subcase occurs for $m = 3$ and $n = 0$, i.e.

$$\langle r^4\rangle\langle r^{-2}\rangle^2 \geqslant \frac{(\alpha_0+6)(\alpha_0+5)(\alpha_0+4)(\alpha_0+3)}{(\alpha_0+2)^2(\alpha_0+1)^2}N^3 \tag{33}$$

where it is already included that the value $\alpha = \alpha_0$ gives the best bound.

D. For $a = \frac{2}{3}$, (5) transforms into

$$\langle r^{n+2m-2}\rangle^2\langle r^{n-2}\rangle \geqslant \frac{[\Gamma(n+\alpha+2m+1)]^2\,\Gamma(n+\alpha+1)}{[\Gamma(n+\alpha 4m/3+1)]^3}\langle r^{n+4m/3-2}\rangle^3 \tag{34}$$

with $m \geqslant 0$, $\alpha \geqslant \alpha_0$ and $n \geqslant -\alpha_0$. A relevant particular subcase occurs for $n = 0$ and $m = 3$, that is

$$\langle r^4\rangle^2\langle r^{-2}\rangle \geqslant \frac{(\alpha_0+6)^2(\alpha_0+5)^2}{(\alpha_0+4)(\alpha_0+3)(\alpha_0+2)(\alpha_0+1)}\langle r^2\rangle^3 \tag{35}$$

where, again, the optimal value $\alpha = \alpha_0$ was taken into account.

Finally, for completeness, let us mention that other sets of inequalities have been published, which involve more than three radial expectation values (Gadre and Matcha 1981, Angulo and Dehesa 1991) and/or the nuclear charge Z (Gálvez and Porras 1991). Among them, particularly connected to this work are the inequalities (Gálvez and Porras 1991)

$$\langle r^{n-3}\rangle \leqslant \frac{2Z}{n}\langle r^{n-2}\rangle \qquad \text{for } n > 0$$

of which some particular cases are

$$\langle r^{-2}\rangle \leqslant 2Z\langle r^{-1}\rangle \qquad \langle r^{-1}\rangle \leqslant Z^2 \qquad \langle r\rangle \geqslant \tfrac{3}{2}$$

for neutral atoms.

To summarize, it has been shown that the spherically averaged electron density $\rho(r)$ of an atomic system in its ground state has the following property: the function $\rho(r)/r^{\alpha_0}$ is logarithmically convex with α_0 given by (1). Secondly, this property has been used to obtain a general, rigorous and compact inequality involving up to three radial expectation values, which includes, as particular cases, all the similar inequalities previously published. Thirdly, by means of the near-Hartree–Fock atomic wavefunctions of Clementi and Roetti, the log-convexity property has been investigated. The analysis of the first 54 neutral atoms shows that α_0 varies non-monotonically with Z, its values going from zero (H, He) to 5.98 (Xe). This indicates that hydrogen and helium are the only two atoms to be logarithmically convex from the origin. Finally, the Hartree–Fock analysis of some of the encountered inequalities shows that the log-convexity of the atomic function $\rho(r)/r^{\alpha_0}$ produces inequalities

of, generally speaking, higher accuracy than those based on either the monotonic decreasing or even the convexity of the electron density $\rho(r)$ for both light and heavy atoms unless expectation values of negative order are involved.

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